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For: TRANSPARENT LAMINATE, METHOD FOR PRODUCING THE SAME, AND PLASMA DISPLAY PANEL

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VERIFIED TRANSLATION OF PRIORITY DOCUMENTS

Sir:

Submitted herewith are the Verified Translation of Priority Document for Japanese Application Number Hei. 11-369355 filed on December 27, 1999 and Japanese Application Number Hei. 2000-383072 filed on December 18, 2000, upon which applications the claim for priority is based.

Respectfully submitted,

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This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Applicant(s):   NITTO DENKO CORPORATION

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[Title of Document] SPECIFICATION

[Title of the Invention] TRANSPARENT LAMINATE, METHOD FOR

PRODUCING THE SAME, AND PLASMA DISPLAY PANEL

[Scope of Claim for a Patent]

[Claim 1] A transparent laminate comprising a transparent

substrate, n thin-film units ($2 \leqq n \leqq 5$) laminated unit by unit

successively on a surface of said substrate, and a

high-refractive-index transparent thin film formed on a surface

of laminate of said n thin-film units, each of said n thin-film

units consisting of a high-refractive-index thin film and a

silver transparent conductor thin film, wherein the standard

deviation of visible light transmittance in a wave range of

from 450 to 650 nm is not larger than 5 %.

[Claim 2] A transparent laminate according to Claim 1,

wherein: each of said silver transparent conductor thin films

has an approximately constant thickness in a range of from 5

to 20 nm; each of the high-refractive-index transparent thin

film located on the surface of said transparent substrate and

the high-refractive-index transparent thin film located in an

outermost layer has a thickness $(5/2) \times (1 \pm 0.15)$ times as large

as the thickness of each of said silver transparent conductor

thin films; and each of the other high-refractive-index

transparent thin films located in an intermediate region between

said high-refractive-index transparent thin film located on

the surface of said transparent substrate and said

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high-refractive-index transparent thin film located as the outermost layer has a thickness $5 \times (1 \pm 0.15)$ times as large as the thickness of each of said silver transparent conductor thin films.

[Claim 3] A transparent laminate according to Claim 1 or 2, further comprising a low-refractive-index transparent thin film formed on said surface of said transparent substrate, said low-refractive-index transparent thin film having a refractive index n_L in a range of from 1.3 to 1.6 and having a thickness of 550 nm $\times (1/4n_L) \times (1 \pm 0.15)$.

[Claim 4] A transparent laminate according to Claim 3, further comprising a low-refractive-index transparent thin film formed on a surface of said high-refractive-index transparent thin film located as the outermost layer, said low-refractive-index transparent thin film having a refractive index n_L in a range of from 1.3 to 1.6 and having a thickness of 550 nm $\times (1/2n_L) \times (1 \pm 0.15)$.

[Claim 5] A transparent laminate according to Claim 3, further comprising any one of an anti-reflection film, an anti-mirroring film and a low-reflection anti-mirroring film stuck onto said surface of said high-refractive-index transparent thin film located as the outermost layer, through a transparent adhesive layer.

[Claim 6] A method for producing a transparent laminate according to any one of Claims 1 through 5, wherein when said

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high-refractive-index transparent thin films and said silver transparent conductor thin films are formed by a vacuum dry process, the temperature T (K) of said transparent substrate at the time of the formation of said films is set to be in a range $330 \leqq T \leqq 390$; and the film-forming rate R (nm/sec) of said silver transparent conductor thin films is set to be R = (1/40) $\times$ (T-300) $\pm$ 0.5.

[Claim 7] A plasma display panel filter using a transparent laminate according to any one of Claims 1 through 5.

[Detailed Description of the Invention]

[0001]

[Technical Field pertinent to the Invention]

The present invention relates to a transparent laminate, a method for producing the transparent laminate, and a plasma display panel (hereinafter referred to as "PDP") filter using the transparent laminate.

[0002]

[Background Art]

Nowadays in the society where information orientation is advancing remarkably, performance required of a display to be used as a terminal for displaying an image is diversified greatly. Especially, a great deal of attention has been paid to a PDP as a novel display succeeding a CRT and a liquid-crystal display because it is easy to increase the size of the PDP while reducing the thickness of the PDP. The PDP has already come

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onto the market.

[0003]

In the PDP, electric discharge is produced in rare gas enclosed in the panel, especially, in gas containing neon as a main component. R, G and B fluorescent materials applied onto cells of the panel are made to emit fluorescence by vacuum ultraviolet rays generated at the electric discharge. In this light emission process, electromagnetic waves and near-infrared rays unnecessary for display on the PDP are emitted simultaneously. The electromagnetic waves need to be cut because they cause malfunctions of peripheral devices and have bad influence on human bodies. The near-infrared rays also need to be cut because there is a problem that remote controllers of household electronic appliances, karaoke, audio-video systems, etc. are made to malfunction by the near-infrared rays because the near-infrared rays have a wave range of from 850 to 1200 nm whereas the remote controllers have a light-receiving sensitivity range of from 700 to 1300 nm.

[0004]

In a transparent laminate of the type having a structure in which a metal thin film is sandwiched between high-refractive-index transparent thin films, both the electrically conducting property and infrared reflecting property of the metal thin film can be utilized and, at the same time, a function of preventing reflection of visible rays

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on a metal surface of the metal thin film can be given to the transparent laminate by the high-refractive-index transparent thin films. Accordingly, such a transparent laminate is adapted to materials capable of transmitting visible rays but reflecting heat rays, such as a transparent heat-insulating material for solar cell, a window material for agricultural green house or building, a food showcase, etc. Further, the transparent laminate exhibits transparency and high electrical conductivity. Accordingly, such a transparent laminate is also adapted to materials such as liquid-crystal display electrodes, electric field light-emitting material electrodes, electromagnetic wave shielding films, anti-static films, etc. The structure of such a transparent laminate has been described in JP-A-55-11804, JP-A-9-176837, etc.

[0005]

[Problem to be solved by the Invention]

However, the aforementioned transparent laminate did not have performance permitting direct use as a PDP filter and, hence, it was unable to satisfy both high electromagnetic wave shielding property and near-infrared cutting property simultaneously. In use as a PDP filter, visible light transmitting property to prevent the display quality of the PDP from being spoiled is required intensively in addition to the aforementioned two properties. Especially, setting the color tone of the filter to neutral gray is required intensively.

Anti-reflection property is further required from the point of view of prevention of mirroring of external light, light emitted from a fluorescent lamp, or the like. It was, however, impossible that these requirements were served by the aforementioned transparent laminate.

[0006]

Particularly to set the color tone of the PDP filter to neutral gray, it is necessary that the transmittance of the PDP filter is kept constant in a visible light range. In the transparent laminate having a metal thin film sandwiched between high-refractive-index transparent thin films, it was not easy to keep the transmittance constant all over the visible light range. For example, an effort was made at adjusting the color tone to neutral gray by adding and uniformly dispersing a dye, or the like, capable of absorbing light with a specific wavelength into the transparent substrate, or the like. It was, however, not easy to adjust finely the respective amounts of a plurality of absorbents to be added and disperse uniformly the absorbents. Hence, there was a problem that a greater part of absorbents lacked durability as well as a high-grade technique was required.

[0007]

Upon such circumstances, an object of the present invention is to provide a transparent laminate which can satisfy all properties such as electromagnetic wave shielding property,

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near-infrared cutting property, visible light transmitting property and visible light low-reflecting property required of a PDP filter in spite of a relatively simple structure of the transparent laminate and which can exhibit a color tone of neutral gray with little dependence of the transmittance of the transparent laminate on wavelengths in a visible light range without use of any absorbent such as dyes, or the like. Another object of the present invention is to provide a light-weight thin PDP filter of good visibility using the transparent laminate.

[0008]

[Means for Solving the Problem]

In the transparent laminate in which metal thin films and high-refractive-index transparent thin films are formed by a vacuum dry process, it is known that each metal thin film with a thickness of from the order of nanometers to the order of tens of nanometers is formed not as a continuous flat film but as an island structure. The process of growth of the metal thin film is affected by the film-forming temperature of the substrate, the film-forming rate, the material of the substrate, the film-forming method, etc. Especially, the process of growth of the metal thin film is apt to be affected by the film-forming temperature and the film-forming rate. Generally, when the temperature of the substrate is high, aggregation is apt to occur in the inside of the thin film. As a result, each

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of islands is shaped like a sphere, so that it is difficult to form a continuous structure even in the case where the thickness of the thin film is relatively large. When the film-forming rate is high, the number of islands increases and hence the density thereof becomes high. As a result, the thin film is easily formed as a continuous structure even in the case where the thickness of the thin film is relatively small ("Thin Film" written by Kinbara et al, published by Shokabo Co., Ltd., 1979).

[0009]

When the metal thin film is formed as an island structure, abnormal light absorption called surface plasma resonance absorption occurs ("Thin Film Handbook" written by Namioka, published by Ohmsha Ltd., 1983). Particularly in the case of a silver transparent conductor thin film, the electromagnetic wave shielding function cannot be fulfilled sufficiently because electric resistance in the direction of width of the film is reduced remarkably as well as visible light transmittance in a certain wave range is reduced greatly by surface plasma resonance absorption. On the other hand, even in the case where the film-forming rate is heightened to form a continuous film almost perfectly, dependence of transmittance on wavelengths is so large that the transparent laminate cannot exhibit the color tone of neutral gray though visible light transmittance is improved as a whole.

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[0010]

On the basis of the aforementioned knowledge, the inventors of the present invention have utilized the following condition when silver transparent conductor thin films suitable as metal thin films are formed on a transparent substrate by a vacuum dry process so that each silver transparent conductor thin film is sandwiched between high-refractive-index transparent thin films. That is, in the condition that the temperature of the transparent substrate is set to be in a predetermined range and the film-forming rate of the silver transparent conductor thin films is set so that there is a specific relationship between the temperature and the film-forming rate, delicate light absorption different from the aforementioned general surface plasma resonance absorption occurs. As a result, wavelength dependence of visible light transmittance is reduced so that the transparent laminate can exhibit the color tone of neutral gray without addition of any absorbent such as a dye into the transparent substrate.

[0011]

Moreover, the transparent laminate produced as described above has transmittance kept sufficiently high with respect to the whole visible light range and can satisfy all properties such as electromagnetic wave shielding property, near-infrared cutting property, visible light low-reflecting property, etc. required of a PDP film in spite of the aforementioned simple

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structure of the transparent laminate. Moreover, it has been found that a light-weight thin PDP filter of good visibility having the aforementioned properties can be obtained by use of the transparent laminate. The findings have resulted in accomplishing the present invention.

[0012]

That is, according to an aspect of the present invention, there is provided a transparent laminate comprising a transparent substrate, n thin-film units $(2 \leqq n \leqq 5)$ laminated unit by unit successively on a surface of the substrate, and a high-refractive-index transparent thin film formed on a surface of laminate of the n thin-film units, each of the n thin-film units consisting of a high-refractive-index thin film and a silver transparent conductor thin film, wherein the standard deviation of visible light transmittance in a wave range of from 450 to 650 nm is not larger than 5 %. In the above transparent laminate, preferably, each of the silver transparent conductor thin films has an approximately constant thickness in a range of from 5 to 20 nm; each of the high-refractive-index transparent thin film located on the surface of the transparent substrate and the high-refractive-index transparent thin film located in an outermost layer has a thickness $(5/2) \times (1 \pm 0.15)$ times as large as the thickness of each of the silver transparent conductor thin films; and each of the other high-refractive-index

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transparent thin films located in an intermediate region between the high-refractive-index transparent thin film located on the surface of the transparent substrate and the high-refractive-index transparent thin film located as the outermost layer has a thickness $5 \times (1 \pm 0.15)$ times as large as the thickness of each of the silver transparent conductor thin films.

[0013]

Incidentally, in this specification, the thickness of each of thin films constituting the transparent laminate, that is, the thickness of each of thin films such as high-refractive-index transparent thin films, silver transparent conductor thin films, etc. provided on the transparent substrate means a thickness (mass thickness) which is set to a predetermined value through measuring the film thickness of a sample subjected to a film-forming process for a long time in one and the same condition (or the thickness of a sample thickened at a low roll speed in the case of roll-to-roll) by a feeler type thickness meter, or the like, and calculating the film-forming time (or roll speed) on the basis of the measured film thickness.

Generally, the film-forming rate in the case of roll-to-roll is often expressed in dynamic film-forming rate (nm·m/sec). In this case, however, the film-forming rate used in the present invention is calculated by R/L (nm/sec) when

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R (nm·m/sec) is the dynamic film-forming rate and L (m) is the length of a sputtering target in the direction of the rotation of a roll. Hence, even in the case where the dynamic film-forming rate is constant, the film-forming rate used in the present invention varies in accordance with the length of the target.

[0014]

In the above transparent laminate, preferably, the laminate further comprises a low-refractive-index transparent thin film formed on the surface of the transparent substrate, the low-refractive-index transparent thin film having a refractive index n_L in a range of from 1.3 to 1.6 and having a thickness of 550 nm× (1/4n_L) × (1±0.15). In the above transparent laminate according, preferably, the laminate further comprises a low-refractive-index transparent thin film formed on a surface of the high-refractive-index transparent thin film located as the outermost layer, the low-refractive-index transparent thin film having a refractive index n_L in a range of from 1.3 to 1.6 and having a thickness of 550 nm× (1/2n_L) × (1±0.15). Further, in place of such a low-refractive-index transparent thin film, the above transparent laminate further comprises any one of an anti-reflection film, an anti-mirroring film and a low-reflection anti-mirroring film stuck onto the surface of the high-refractive-index transparent thin film located as the outermost layer, through a transparent adhesive layer.

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Accordingly, the transparent laminate configured as described above can be provided as a surface mar-proof transparent laminate without spoiling optical performance.

[0015]

Further, according to another aspect of the present invention, there is provided a method for producing any one of the transparent laminates mentioned above, wherein when the high-refractive-index transparent thin films and the silver transparent conductor thin films are formed by a vacuum dry process, the temperature T (K) of the transparent substrate at the time of the formation of said films is set to be in a range $330 \leqq T \leqq 390$; and the film-forming rate R (nm/sec) of the silver transparent conductor thin films is set to be R = (1/40) $\times$ (T-300) $\pm$0.5. Hence, delicate light absorption occurs in the silver transparent conductor thin films, so that the standard deviation of visible light transmittance in a wave rage of from 450 to 650 nm is set to be not larger than 5 %. Thus, the transparent laminate can be provided as a transparent laminate which is small in wavelength dependence of visible light transmittance and which exhibits the color tone of neutral gray.

[0016]

The present invention further relates to a PDP filter using the transparent laminate configured as described above. Generally, a transparent adhesive layer is preferably formed on a rear surface of the transparent laminate configured as

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described above so that the transparent laminate can be used as a PDP filter. In practical use, the PDP filter may be directly stuck onto a front display glass portion of a PDP through the transparent adhesive layer to thereby form a direct-sticking type PDP display device. As another usage, the aforementioned PDP filter may be stuck onto a surface (opposite to the PDP) of a transparent molded material disposed on the front side of the PDP through an air layer to thereby form a PDP front plate.

[0017]

[Mode for Carrying out the Invention]

An example of a transparent laminate according to the present invention and an example of a PDP filter using the transparent laminate will be described below specifically with reference to Figs. 1 and 2.

[0018]

Fig. 1 shows an example of the transparent laminate according to the present invention. Thin-film units (for example, three thin-film units in Fig. 1) each consisting of a combination of a high-refractive-index transparent thin film and a silver transparent conductor thin film are laminated repetitively successively on a surface of a transparent substrate 1. That is, in Fig. 1, high-refractive-index transparent thin films (2A, 2B and 2C) and silver transparent conductor thin films (3A, 3B and 3C) are laminated repetitively

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successively on the surface of the transparent substrate 1. A high-refractive-index transparent thin film 2D is further formed as the outermost layer on a surface of the silver transparent conductor thin film 3C. The present invention is characterized in that the standard deviation of visible light transmittance in a wave range of from 450 to 650 nm is set to be not larger than 5 %, preferably not larger than 4 %, especially not larger than 3 % (generally 1 %).

[0019]

In the transparent laminate, the thickness of each of the silver transparent conductor thin films (3A, 3B and 3C) is set to be approximately constant in a range of from 5 to 20 nm. The thickness of each of the high-refractive-index thin films 2A and 2D located on the surface of the transparent substrate 1 and located as the outermost layer is set to be $(5/2) \times (1 \pm 0.15)$ times as large as the thickness of each of the silver transparent conductor thin films (3A, 3B and 3C). The thickness of each of the other high-refractive-index transparent thin films (2B and 2C) located in an intermediate region is set to be $5 \times (1 \pm 0.15)$ times as large as the thickness of each of the silver transparent conductor thin films (3A, 3B and 3C).

[0020]

Incidentally, the high-refractive-index transparent thin films (2A, 2B, 2C and 2D) may be formed of the same material

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or may be formed of different materials respectively.

Similarly, the silver transparent conductor thin films (3A,

3B and 3C) may be formed of the same material or may be formed

of different materials respectively. Although the

aforementioned example has been described upon the case where

three thin-film units each consisting of a combination of a

high-refractive-index transparent thin film and a silver

transparent conductor thin film are laminated repetitively,

the number $\underline{n}$ of repeated units can be selected suitably from

the range $2 \leqq n \leqq 5$. If the number $\underline{n}$ of repeated units is smaller

than 2, both electromagnetic wave shielding property and

near-infrared cutting property become insufficient. If the

number $\underline{n}$ is larger than 5, it is difficult to obtain a desired

result in terms of optical characteristic because of lowering

of visible light transmittance, or the like.

[0021]

Fig. 2 shows a modified example of the transparent laminate

shown in Fig. 1. As shown in Fig. 2, a low-refractive-index

transparent thin film 4A having a refractive index n_L in a range

of from 1.3 to 1.6 and having a thickness of 550 nm $\times$ (1/4n_L)

$\times$ (1$\pm$0.15) with respect to the optical center wavelength λ

= 550 nm is formed on the surface of the transparent substrate

1, that is, inserted in between the transparent substrate 1

and the high-refractive-index transparent thin film 2A. A

low-refractive-index transparent thin film 4B having a

refractive index n_L in a range of from 1.3 to 1.6 and having

a thickness of 550 nm$\times$(1/2n_L)$\times$(1$\pm$0.15) with respect to the

optical center wavelength λ = 550 nm is further formed on the

surface of the high-refractive-index transparent thin film 2D

located as the outermost layer. The other configuration is

quite the same as that in Fig. 1.

[0022]

When, for example, the thickness of each of the silver

transparent conductor thin films (3A, 3B and 3C) is selected

to be 13 nm and the refractive index n_L of each of the

low-refractive-index transparent thin films (4A and 4B) is

selected to be 1.4 in the respective transparent laminates shown

in Figs. 1 and 2, the thicknesses of the respective thin films

are determined, rounded off to one decimal place, as follows.

High-refractive-index transparent thin films 2A, 2D:

32.5nm$\pm$4.9nm

High-refractive-index transparent thin films 2B, 2C:

65.0nm$\pm$9.8nm

Silver transparent conductor thin films 3A, 3B, 3C:

13nm (approximately constant)

Low-refractive-index transparent thin film 4A:

98.2nm$\pm$14.7nm

Low-refractive-index transparent thin film 4B:

196.4nm$\pm$29.5nm

[0023]

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The transparent laminate configured as described above according to the present invention can satisfy all properties such as electromagnetic wave shielding property, near-infrared cutting property, visible light transmitting property, visible light low-reflecting property, etc. required of a PDP filter in spite of the aforementioned simple configuration of the transparent laminate. Moreover, the transparent laminate fulfills an excellent effect that the transparent laminate exhibits the color tone of neutral gray without addition of any absorbent such as dyes into the transparent substrate because the dependence of visible light transmittance on wavelengths is small.

[0024]

The transparent laminate can be produced as follows. That is, when the high-refractive-index transparent thin films (2A, 2B, 2C and 2D) and the silver transparent conductor thin films (3A, 3B and 3C) are formed by a vacuum dry process, the condition is set such that the film-forming temperature T (K) of the transparent substrate is set to be in a range $330 \leqq T \leqq 390$ and the film-forming rate R (nm/sec) of the silver transparent conductor thin films (3A, 3B and 3C) is set to be R = $(1/40) \times (T-300) \pm 0.5$. According to this method, it is possible to obtain a transparent laminate which satisfies all the aforementioned properties required of a PDP filter. Further, the transparent laminate exhibits the color tone of neutral

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gray with small dependence of visible light transmittance on wavelengths so that delicate light absorption occurs in the silver transparent conductor thin films and the standard deviation of visible light transmittance in a wave range of from 450 to 650 nm is not larger than 5 %.

[0025]

On the contrary, if the film-forming temperature T of the transparent substrate is out of the aforementioned range or if the film-forming rate R of the silver transparent conductor thin films is out of the aforementioned range, it is impossible to obtain a transparent laminate which satisfies all the aforementioned properties and which exhibits the color tone of neutral gray. Particularly if the film-forming rate R is lower than the aforementioned range, visible light transmittance is lowered greatly because each of the silver transparent conductor thin films is shaped like an island structure so that the silver transparent conductor thin film exhibits large absorption in a visible light range. If the film-forming rate R is higher than the aforementioned range, the transparent laminate cannot exhibit the color tone of neutral gray because the dependence of transmittance on wavelengths becomes large though each of the silver transparent conductor thin films is formed as a continuous film almost perfectly so that visible light transmittance is improved as a whole.

[0026]

In the producing method according to the present invention, the temperature T of the transparent substrate can be controlled by applying tension to the transparent substrate to bring the transparent substrate into close contact with a main roll which is adjusted by a heating medium flowing in the inside when, for example, film formation is performed by roll-to-roll. The film-forming rate R of each of the silver transparent conductor thin films can be controlled by adjusting electric power to be applied to the target of the silver transparent conductor thin film, for example, in the case of a sputtering method. The film-forming rate can be calculated on the basis of the roll speed and the length of a region on which the silver transparent conductor thin film is deposited as vapor by the sputtering method.

[0027]

A material exhibiting transparency in a visible light range and a certain degree of surface smoothness can be used as the transparent substrate 1 to be used in the present invention. For example, polyethylene terephthalate, triacetyl cellulose, polyethylene naphthalate, polyether-sulfone, polycarbonate, polyacrylate, polyether-ether-ketone, or the like, may be preferably used. The thickness of the transparent substrate is not particularly limited if there is no problem of thermal creasing in the dry process. Generally, the thickness of the transparent laminate is preferably set to be in a range of from

10 to 250 μm. Beside the aforementioned high-molecular film, a film having either surface or both surfaces coated with a hard coat layer may be used. The transparent layer 1 may be of an ultraviolet-curing type or of a heat-curing type, and the thickness thereof is preferably in a range of from 1 to 10 μm.

[0028]

Any high-refractive-index optical film material can be used to some degree as the material of the high-refractive-index transparent thin films (2A, 2B, 2C and 2D). Preferably, a thin film material having a refractive index in a range of from 1.9 to 2.5 may be used. The material may be a single high-refractive-index transparent material or may be formed by sintering a plurality of high-refractive transparent materials. A material having an effect of preventing migration of silver or having an effect of making a barrier to water and oxygen is preferred more especially. Examples of the preferred material are: a material containing indium oxide as a main component and containing titanium dioxide, and further containing a small amount of tin oxide and cerium dioxide; titanium dioxide; zirconium oxide; zinc sulfide; bismuth oxide; niobium pentoxide; and so on. These thin films are formed by a vacuum dry process such as sputtering, vacuum vapor deposition, ion-plating, etc.

[0029]

The material of the silver transparent conductor thin films (3A, 3B and 3C) is constituted by a combination of 90 % by weight or more of silver and one member or two or more members selected from the group consisting of gold, copper, palladium, platinum, manganese and cadmium. The preferred is a solid solution material composed of 90 % by weight to 99 % by weight of silver and 1 % by weight to 10 % by weight of the aforementioned metal. Especially, a solid solution material of silver containing 1 % by weight to 10 % by weight of gold is preferred from the point of view of prevention of deterioration of silver. If the amount of gold mixed with silver is larger than 10 % by weight, it is difficult to obtain a low resistance value because of increase of specific resistance. If the amount of gold is smaller than 1 % by weight, silver is apt to deteriorate. The silver transparent conductor thin films constituted by these materials are formed by a vacuum dry process such as sputtering, or the like. As described above, the thickness of each of the silver transparent conductor thin films is set to be in a range of from 5 to 20 nm, preferably in a range of from 9 to 17 nm, especially in a range of from 11 to 14 nm.

[0030]

A low-refractive-index optical material transparent to light in a visible light range can be used as the material of the low-refractive-index transparent thin films (4A and 4B). The preferred is a thin film material having a refractive index

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in a range of from 1.3 to 1.6. The thin films may be formed by a vacuum dry process such as sputtering, vacuum vapor deposition, ion-plating, or the like, or may be formed by a wet process such as gravure coating, micro-gravure coating, reverse coating, dip coating, or the like. The temperature of the transparent substrate 1 when the low-refractive-index transparent thin films (4A and 4B) is formed is not particularly defined. Even in the case where the low-refractive-index transparent thin films (4A and 4B) are formed at room temperature, the characteristic of the present invention is not disturbed at all.

[0031]

A material permitting good contact between the transparent substrate 1 and the high-refractive-index transparent thin film 2A is preferably used as the material of the low-refractive-index thin film 4A. An easy bonding process such as a process of providing a primer layer on a surface of the transparent substrate 1 may be made. Examples of the preferred material are magnesium fluoride, silicon dioxide, fluorine-containing silicon oxide, heat-curing or ultraviolet-curing fluorine high-molecular materials, heat-curing or ultraviolet-curing silicone high-molecular materials, etc.

[0032]

The low-refractive-index transparent thin film 4B may

be made of the same material as the material of the low-refractive-index transparent thin film 4A or may be made of a material different therefrom. A material excellent in mar-proofness is preferably used so that the low-refractive-index transparent thin film 4B can serve as an overcoat layer on the outermost side. For this reason, the low-refractive-index transparent thin film 4B is preferably formed to be as thick as possible. According to the present invention, the film can be thickened more greatly as the refractive index decreases. Hence, a material having a refractive index as low as possible is preferably used. A material permitting the low-refractive-index transparent thin film 4B itself to have anti-contamination property may be used more preferably or an anti-contamination layer with a thickness of 10 nm or smaller may be formed on a surface of the low-refractive-index transparent thin film 4B. Examples of the preferred material are magnesium fluoride, silicon dioxide, fluorine-containing silicon oxide, heat-curing or ultraviolet-curing fluorine high-molecular materials, heat-curing or ultraviolet-curing silicone high-molecular materials, etc.

[0033]

In the present invention, for example, in the transparent laminate shown in Fig. 2, the formation of the low-refractive-index transparent thin film 4B may be omitted.

Further, an anti-reflection film, an anti-mirroring film or a low-reflection anti-mirroring film may be stuck, in place of the formation of the low-refractive-index transparent thin film 4B, onto a surface of the high-refractive-index transparent thin film 3C located as the outermost layer through a transparent adhesive layer. Also in this case, a transparent laminate excellent in surface mar-proofness can be obtained without spoiling optical performance, or the like. As each of the aforementioned films, there can be used any kind of known film which is constituted by a film substrate such as a polyester film or a triacetyl cellulose film, and a single or multi-layer such as an anti-reflection film, an anti-mirroring layer or a low-reflection anti-mirroring layer provided on the film substrate.

[0034]

With respect to various transparent laminates configured as described above according to the present invention, generally, a transparent adhesive layer is formed on the rear surface side of the transparent laminate, that is, on the rear surface side of the transparent substrate 1 so that the transparent laminate can be used as a light-weight thin PDP filter of good visibility having the aforementioned properties. In practical use, the PDP filter may be directly stuck onto a front display glass portion of a PDP through the transparent adhesive layer to thereby form a direct-sticking type PDP display device.

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Alternatively, the PDP filter may be stuck, through the transparent adhesive layer, onto a surface (opposite to the PDP) of a transparent molded material disposed on the front side of the PDP through an air layer to thereby form a PDP front plate.

[0035]

The former direct-sticking type PDP display device can contribute to prevention of scattering of glass, reduction in weight, size and cost of the PDP itself, etc. Moreover, the problem of increase of visible light reflectivity, double reflection, etc. caused by excessive interfacial reflection can be solved because the air layer low in refractive index can be eliminated compared with the case where the PDP front plate is disposed. Hence, visibility of the PDP can be improved remarkably. On the other hand, the latter PDP front plate can be particularly adapted to the case where a glass member to be used in the PDP has a problem in shortage of strength, etc.

[0036]

[Examples]

The present invention will be described below more specifically on the basis of examples thereof while the present invention is not limited to the following examples.

[0037]

Example 1

Three thin-film units each unit consisting of a

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combination of a high-refractive-index transparent thin film and a silver transparent conductor thin film were formed successively on one side of a 125 μm-thick transparent polyethylene terephthalate (hereinafter referred to as "PET") film by a DC magnetron sputtering method. A high-refractive-index transparent thin film was further formed on a surface of the laminate of the three thin-film units. Thus, a transparent laminate was produced by the aforementioned method. In this occasion, In_2O_3 containing 12.6 % by weight of TiO_2 (hereinafter abbreviated as "IT") was used as a target material for forming the high-refractive-index transparent thin films and Ag containing 5 % by weight of Au (hereinafter abbreviated as "Ag") was used as a target material for forming the silver transparent conductor thin films.

[0038]

Film thickness was controlled by use of the analytical curve of the film-forming rate obtained on the basis of film thickness measured by a surface roughness meter (DEKTAK3) attached to a thick film. As an example, when DC power of 3 W/cm^2 was applied as sputtering power to the IT target and DC power of 0.55 W/cm^2 was applied as sputtering power to the Ag target, the film-forming rate of IT was 1.6 nm/sec and the film-forming rate of Ag was 1.8 nm/sec. Each film-forming rate was approximately proportional to the sputtering power. The length of the Ag target used in Example 1 was 16 cm. Hence,

the roll speed for forming an Ag film with a thickness of 13nm was determined to be [1.8 (nm/sec) ×0.16 (m)]/13 (nm) = 0.0222 (m/sec) = 1.329 (m/min). Thin films with predetermined thicknesses were formed by a roll-to-roll sputtering apparatus. Further, the roll temperature was controlled by adjustment of the temperature of a heating medium circulating in the inside.

[0039]

In the aforementioned method, the roll temperature (equivalent to the temperature of the PET film which was the transparent substrate) and the film-forming rate of Ag were set as follows to produce three kinds of transparent laminates as samples (1) to (3). The thicknesses of respective thin films in these transparent laminates were as shown in numerical values (unit: nm) put in the following parentheses.

Sample (1): PET/IT(32.5)/Ag(13)/IT(65)/Ag(13)/IT
(65)/Ag(13)/IT(32.5)

<Roll Temperature: 373 K,

the film-forming temperature of Ag: 1.8 nm/sec>

Sample (2): PET/IT(32.5)/Ag(13)/IT(65)/Ag(13)/IT
(65)/Ag(13)/IT(32.5)

<Roll Temperature: 353 K,

the film-forming temperature of Ag: 1.3 nm/sec>

Sample (3): PET/IT(32.5)/Ag(13)/IT(65)/Ag(13)/IT
(65)/Ag(13)/IT(32.5)

<Roll Temperature: 333 K,

the film-forming temperature of Ag: 0.8 nm/sec>

[0040]

Comparative Example 1

Transparent laminates as samples (4) and (5) were produced in the same manner as that in Example 1 except that the roll temperature and the film-forming rate of Ag were set as follows. That is, three thin-film units each consisting of a combination of an IT thin film and an Ag thin film were formed successively on a PET film, and an IT thin film was further formed on a surface of the laminate of the three thin-film units. These transparent laminates were examples in which the film-forming rate of Ag was higher than the range defined by the present invention. The thicknesses of respective thin films were as shown in numerical values (unit: nm) put in the following parentheses.

Sample (4): PET/IT(32.5)/Ag(13)/IT(65)/Ag(13)/IT

(65)/Ag(13)/IT(32.5)

<Roll Temperature: 333 K,

the film-forming temperature of Ag: 2.0 nm/sec>

Sample (5): PET/IT(32.5)/Ag(13)/IT(65)/Ag(13)/IT

(65)/Ag(13)/IT(32.5)

<Roll Temperature: 373 K,

the film-forming temperature of Ag: 3.0 nm/sec>

[0041]

Comparative Example 2

Transparent laminates as samples (6) and (7) were produced

in the same manner as that in Example 1 except that the roll temperature and the film-forming rate of Ag were set as follows. That is, three thin-film units each consisting of a combination of an IT thin film and an Ag thin film were formed successively on a PET film, and an IT thin film was further formed on a surface of the laminate of the three thin-film units. These transparent laminates were examples in which the film-forming rate of Ag was higher than the range defined by the present invention. The thicknesses of respective thin films were as shown in numerical values (unit: nm) put in the following parentheses.

Sample (6): PET/IT(32.5)/Ag(13)/IT(65)/Ag(13)/IT

(65)/Ag(13)/IT(32.5)

<Roll Temperature: 373 K,

the film-forming temperature of Ag: 0.8 nm/sec>

Sample (7): PET/IT(32.5)/Ag(13)/IT(65)/Ag(13)/IT

(65)/Ag(13)/IT(32.5)

<Roll Temperature: 333 K,

the film-forming temperature of Ag: 0.1 nm/sec>

[0042]

Transmission spectra expressing optical characteristics of the respective transparent laminates shown in the sample (1) according to Example 1, the sample (4) according to Comparative Example 1 and the sample (6) according to Comparative Example 2 were examined and shown in Fig. 3. It was apparent from the results shown in Fig. 3 that the transparent laminate

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shown in the sample (1) according to Example 1 had flat

characteristic and exhibited the color tone of neutral gray

because the wavelength dependence of transmittance in a visible

light range was small.

[0043]

On the contrary, the transparent laminate shown in the

sample (4) according to Comparative Example 1 with the

film-forming rate of Ag higher than the range defined by the

present invention was obtained as a transparent laminate high

in transmittance as a whole but could not be used suitably as

a PDP filter because the transparent laminate had high

transmittance to a wavelength of 500 nm and exhibited the color

tone of green. Further, the transparent laminate shown in the

sample (6) according to Comparative Example 2 with the

film-forming rate of Ag lower than the range defined by the

present invention was so large in absorption that the

transmittance of a filter was lowered remarkably conversely

to the transparent laminate shown in the sample (4) according

to Comparative Example 1. Also the transparent laminate shown

in the sample (6) could not be used suitably as a PDP filter

because the transparent laminate exhibited the color tone of

dark blue.

[0044]

Then, the PDP filter characteristics of the transparent

laminates shown in the samples (1) to (7) according to Example

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1 and Comparative Examples 1 and 2 were examined and shown in Table 1 (Example) and Table 2 (Comparative Example). In the two Tables, surface resistance values were measured by use of "Lorester SP" made by Mitsubishi Petrochemical Co., Ltd. The optical characteristics of the transparent laminates were measured by use of "U-3410" made by Hitachi, Ltd. Especially, the measurement of reflectivity was performed in the condition that the surface of the transparent laminate having no thin film formed thereon was painted with black. Further, visible light transmittance and visible light reflectivity were calculated on the basis of the obtained transmission and reflection spectra in accordance with JIS R-3016. In the color tone of transmitted light, "ND" means neutral gray, "G" means green, and "DB" means dark blue.

[0045]

TABLE 1

		Example		
Sample Number		(1)	(2)	(3)
Surface Resistance (Ω/□)		1.6	1.6	1.6
Visible Light Transmittance (%)	Wavelength: 450 nm	54.8	55.9	54.8
	Wavelength: 500 nm	56.5	57.7	58.0
	Wavelength: 550 nm	57.7	58.8	59.4
	Wavelength: 600 nm	56.7	57.7	58.2
	Wavelength: 650 nm	52.6	53.1	53.7
	Standard Deviation	2.0	2.2	2.4
Average Luminosity Transmittance (%)		57.0	58.1	58.3
Near-Infrared Cutting Rate (%) <wavelength: 850 nm>		95.6	95.2	95.1
Average Luminosity Reflectivity (%)		2.7	2.8	2.7
Color Tone of Transmitted Light		ND	ND	ND

[0046]

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TABLE 2

		Comparative Example			
		(4)	(5)	(6)	(7)
Sample Number		(4)	(5)	(6)	(7)
Surface Resistance (Ω/□)		1.8	1.5	4.6	2.4
Visible Light Transmittance (%)	Wavelength: 450 nm	63.8	62.1	47.3	54.7
	Wavelength: 500 nm	69.8	68.8	38.3	48.2
	Wavelength: 550 nm	66.7	66.1	34.0	45.4
	Wavelength: 600 nm	61.8	60.8	31.0	42.8
	Wavelength: 650 nm	52.9	53.9	25.6	38.1
	Standard Deviation	6.4	5.7	8.2	6.2
Average Luminosity Transmittance (%)		65.3	64.3	33.8	45.0
Near-Infrared Cutting Rate (%) <wavelength: 850 nm>		95.4	95.1	97.4	91.2
Average Luminosity Reflectivity (%)		2.7	2.6	2.8	2.9
Color Tone of Transmitted Light		G	G	DB	DB

[0047]

It was apparent from the results shown in Table 1 that each of the transparent laminates shown in the samples (1) to (3) according to Example 1 was a transparent laminate which exhibited the color tone of neutral gray because the standard deviation of visible light transmittance in a wave range of from 450 to 650 nm was not larger than 5 % and which can sufficiently satisfy basic characteristics, such as surface resistance, near-infrared cutting rate, visible light transmittance and visible light reflectivity, essential to a PDP filter.

[0048]

On the contrary, each of the transparent laminates shown in the samples (4) to (7) according to Comparative Examples 1 and 2 exhibited the color tone of green or dark blue because the standard deviation of visible light transmittance in a wave

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range of from 450 to 650 nm was larger than 5 %. Particularly in the transparent laminates shown in the samples (6) and (7) according to Comparative Example 2, remarkable lowering of transmittance and increase of surface resistance were observed simultaneously. It was conceived that this was owing to the fact that an island structure remained in each of the silver transparent conductor thin films because the silver transparent conductor thin film was not perfectly formed as a continuous film.

[0049]

Example 2

An SiO$_2$ layer was formed on a 125 μm-thick transparent PET film at room temperature by a vacuum vapor deposition method. The refractive index n$_L$ of SiO$_2$ measured by an ellipsometer was 1.45. The thickness of the SiO$_2$ layer was set to be 95 nm. Three thin-film units each consisting of a combination of an IT thin film and an Ag thin film were formed successively on a surface of the SiO$_2$ layer in the same manner as in Example 1. An IT thin film was further formed on a surface of the laminate of the three thin-film units. Thus, a transparent laminate was produced as a sample (8). The thicknesses of respective thin films were as shown in numerical values (unit: nm) put in the following parentheses. The roll temperature for forming the IT thin films and the Ag thin films and the film-forming rate of Ag were as follows.

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Sample (8): PET/SiO$_2$(95)/IT(32.5)/Ag(13)/IT(65)/

Ag(13)/IT(65)/Ag(13)/IT(32.5)

<Roll Temperature: 373 K,

the film-forming temperature of Ag: 1.8 nm/sec>

[0050]

Example 3

In the transparent laminate produced in Example 2, an SiO$_2$ layer was formed on a surface of the IT thin film located as the outermost layer at room temperature by a vacuum vapor deposition method so that the thickness of the SiO$_2$ layer was set to be 190 nm. Thus, a transparent laminate was produced as a sample (9). The thicknesses of respective thin films were as shown in numerical values (unit: nm) put in the following parentheses.

Sample (9): PET/SiO$_2$(95)/IT(32.5)/Ag(13)/IT(65)/

Ag(13)/IT(65)/Ag(13)/IT(32.5)/ SiO$_2$(190)

[0051]

Example 4

In the transparent laminate produced in Example 2, an available anti-reflection film (tradename: "REARLOOK 2200" made by Nippon Oils & Fats Co., Ltd.) was stuck onto a surface of the IT thin film located as the outermost layer through a transparent adhesive agent. Thus, a transparent laminate was produced as a sample (10). The thicknesses of respective thin films were as shown in numerical values (unit: nm) put in the

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following parentheses.

Sample (10): PET/SiO$_2$(95)/IT(32.5)/Ag(13)/IT(65)

/Ag(13)/IT(65)/Ag(13)/IT(32.5)

/Transparent Adhesive Layer

/Anti-Reflection Film

[0052]

Comparative Example 3

A transparent laminate as a sample (11) was produced in the same manner as that in Example 3 except that the formation of the 95 nm-thick SiO$_2$ film on the surface side of the transparent PET film was omitted. The thicknesses of respective thin films were as shown in numerical values (unit: nm) put in the following parentheses.

Sample (11): PET/IT(32.5)/Ag(13)/IT(65)/Ag(13)

/IT(65)/Ag(13)/IT(32.5)/SiO$_2$(190)

[0053]

Comparative Example 4

A transparent laminate as a sample (12) was produced in the same manner as that in Example 4 except that the formation of the 95 nm-thick SiO$_2$ film on the surface side of the transparent PET film was omitted. The thicknesses of respective thin films were as shown in numerical values (unit: nm) put in the following parentheses.

Sample (12): PET/IT(32.5)/Ag(13)/IT(65)/Ag(13)/

IT(65)/Ag(13)/IT(32.5)

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/Transparent Adhesive Layer

/Anti-Reflection Film

[0054]

The PDP filter characteristics of the transparent laminates shown in the samples (8) to (10) according to Examples 2 to 4 and the samples (11) and (12) according to Comparative Examples 3 and 4 were examined in the same manner as described above. Results of the examination were as shown in Table 3. Incidentally, the surface resistance values were measured at a point of time when the IT thin film located as the outermost layer was formed. The description of the surface resistance values on Table 3 was, however, omitted because the surface resistance values were 1.6 $\Omega/\square$ in all the samples without exception. Further, a mar-proof test was performed as follows. The surface of each transparent laminate was rubbed ten times with #0000 steel wool under a load of 2.45×10^{-4} N/m^2. The degree of scars on the surface was observed by eyes. Absence of any scar was evaluated as $\bigcirc$ and presence of some scar was evaluated as $\times$. Results of the evaluation were also shown in Table 3.

[0055]

TABLE 3

		Example			Compara-tive Example	
Sample Number		(8)	(9)	(10)	(11)	(12)
Mar-Proofness		×	○	○	○	○
Visible Light Trans-mittance (%)	Wavelength: 450 nm	55.9	52.5	50.9	51.4	48.8
	Wavelength: 500 nm	57.5	55.9	54.2	54.2	51.5
	Wavelength: 550 nm	58.8	56.3	54.7	53.9	50.7
	Wavelength: 600 nm	57.9	55.0	53.4	53.4	51.2
	Wavelength: 650 nm	53.5	51.4	49.9	50.4	48.4
	Standard Deviation	2.1	2.2	2.1	1.7	1.4
Average Luminosity Transmittance (%)		58.1	55.9	53.2	52.8	49.7
Near-Infrared Cutting Rate (%) <wavelength: 850 nm>		95.5	96.3	97.1	96.8	96.9
Average Luminosity Reflectivity (%)		0.9	2.7	2.9	4.8	7.1
Color Tone of Transmitted Light		ND	ND	ND	ND	ND

[0056]

From the results shown in Table 3, each of the transparent laminates shown in the samples (8) to (10) according to Examples 2 to 4 was small in the standard deviation of visible light transmittance in a wave range of from 450 to 650 nm and exhibited the color tone of neutral gray. Of these, the transparent laminate shown in the sample (8) according to Example 2 had a low average luminosity reflectivity of 0.9 % and was superior in use as a PDP filter from the point of view of prevention of mirroring of external light or light emitted from a fluorescent lamp but was inferior in surface mar-proofness. The surface mar-proofness as well as the average luminosity reflectivity of the transparent laminates were suppressed to be not larger than 3 % in the transparent laminate shown in

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the sample (9) according to Example 3 and having SiO_2 formed as a protective layer on a surface of the IT thin film located as the outermost layer of the transparent laminate shown in the sample (8), and in the transparent laminate shown in the sample (10) according to Example 4 and having an available anti-reflection film stuck onto the surface of the IT thin film.

[0057]

Also each of the transparent laminates shown in the samples (11) and (12) according to Comparative Examples 3 and 4 was small in the standard deviation of visible light transmittance in a wave range of from 450 to 650 nm and exhibited the color tone of neutral gray. In the transparent laminate shown in the sample (11) according to Comparative Example 3, however, SiO_2 was not formed on a surface of the transparent substrate but formed as a protective layer on a surface of the IT thin film located as the outermost layer. Similarly, in the transparent laminate shown in the sample (12) according to Comparative Example 4, SiO_2 was not formed on a surface of the transparent substrate but an available anti-reflection film was stuck as a protective layer onto a surface of the IT thin film located as the outermost layer. Hence, the average luminosity reflectivity of each of the transparent laminates shown in the samples (11) and (12) exceeded 3 % so that visibility of the PDP was blocked remarkably though the transparent laminates satisfied surface mar-proofness.

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[0058]

[Effect of the Invention]

As described above, according to the present invention, the following condition is set when silver transparent conductor thin films are formed on a transparent substrate by a vacuum dry process so that each of the silver transparent conductor thin films is sandwiched between high-refractive-index transparent thin films. In the condition that the temperature of the transparent substrate is set to be in a predetermined range, the film-forming rate of the silver transparent conductor thin films is controlled so that there is a specific relationship between the temperature and the film-forming rate. As a result, there can be provided a transparent laminate which satisfies all properties such as electromagnetic wave shielding property, near-infrared cutting property, visible light transmitting property and visible light low-reflecting property required of a PDP filter in spite of a relatively simple structure of the transparent laminate and which is easy to have surface mar-proofness and small in wavelength dependence of transmittance in a visible light range so that the transparent laminate exhibits the color tone of neutral gray without use of any absorbent such as a dye. A light-weight thin PDP filter of good visibility can be provided by use of the transparent laminate.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 is a sectional view showing an example of a transparent laminate according to the present invention.

[Fig. 2]

Fig. 2 is a sectional view showing another example of a transparent laminate according to the present invention.

[Fig. 3]

Fig. 3 is a characteristic graph showing optical characteristic of the transparent laminate in each of samples (1), (4) and (6) according to Example 1 and Comparative Example 1 and 2.

[Description of the Reference Numerals]
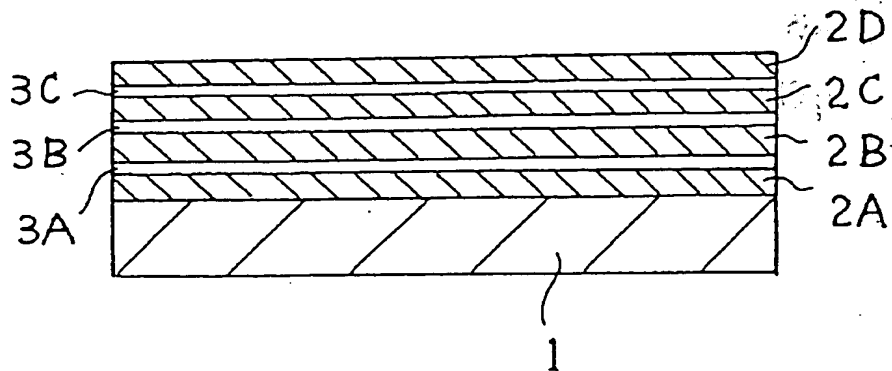
1: transparent substrate

2A, 2B, 2C, 2D: high-refractive-index transparent thin film

3A, 3B, 3C: silver transparent conductor thin film

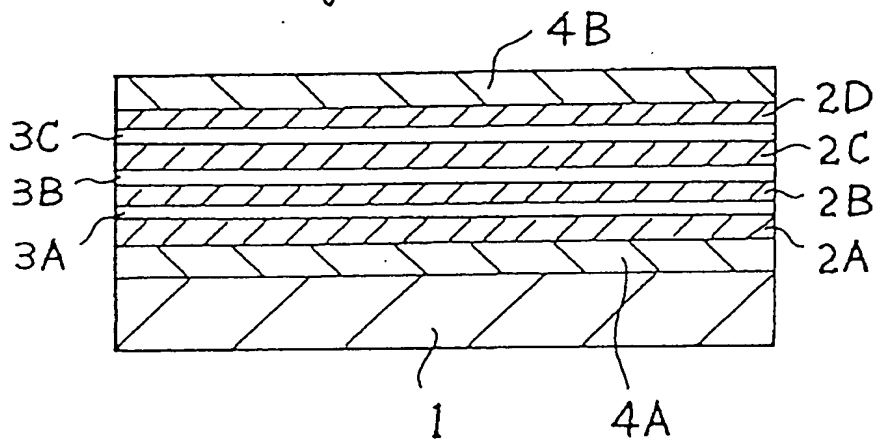4A, 4B: low-refractive-index transparent thin film

Fig-1

1: transparent substrate

2A, 2B, 2C, 2D: high-refractive-index transparent thin film

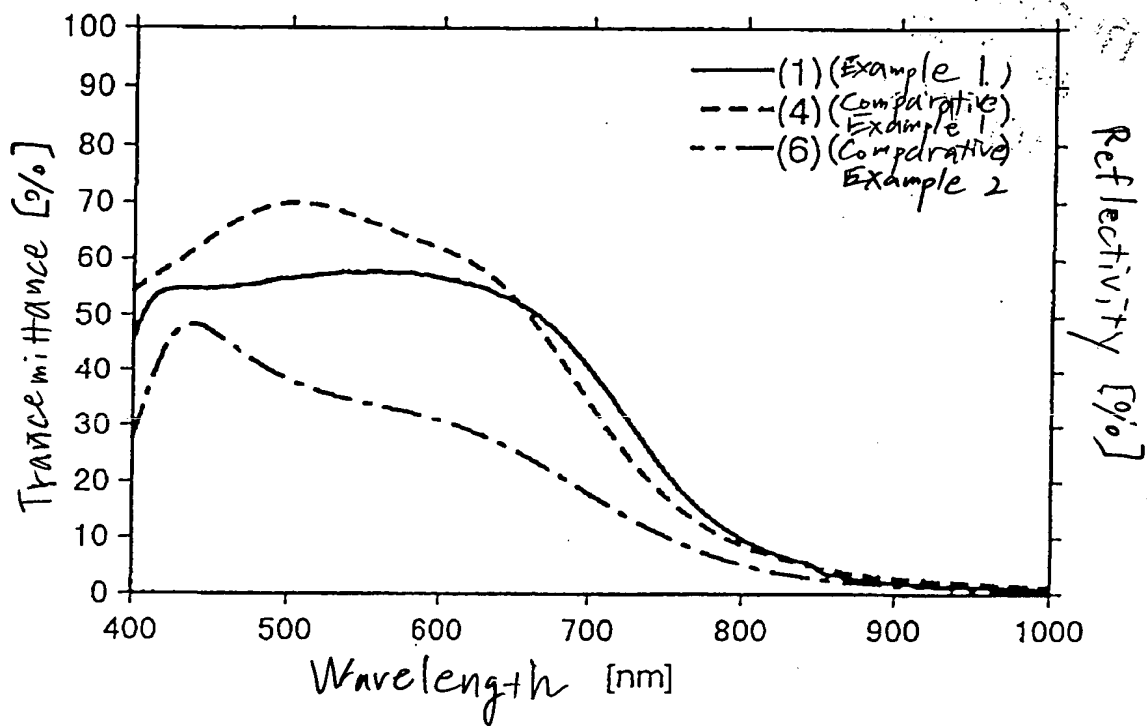3A, 3B, 3C: silver transparent conductor thin film

Fig-2

4A, 4B: low-refractive-index transparent thin film

Fig. 3

Legend:
- (1) (Example 1)
- (4) (Comparative) Example 1
- (6) (Comparative) Example 2

Y-axis (left): Trancemittance [%]
Y-axis (right): Reflectivity [%]
X-axis: Wavelength [nm]

[Title of Document] ABSTRACT

[Abstract]

[Problem] To provide a transparent laminate which satisfies all the electromagnetic wave shielding property, near-infrared cutting property, visible light transmitting property and visible light low-reflecting property, and which exhibits a color tone of neutral gray with little dependence of the transmittance of the transparent laminate on wavelengths in a visible light range.

[Solving Means] In a transparent laminate in which n thin-film units ($2 \leqq n \leqq 5$) are laminated unit by unit successively on a surface of a substrate 1, and a high-refractive-index transparent thin film 2D is formed on a surface of the laminate of the n thin-film units, each of the n thin-film units consisting of a high-refractive-index thin film 2A and a silver transparent conductor thin film 3A, when the high-refractive-index transparent thin films (2A-2D) and the silver transparent conductor thin films (3A-3C) are formed by a vacuum dry process, the temperature T (K) of the transparent substrate 1 at the time of film formation is set to be in a range $330 \leqq T \leqq 390$, and the film-forming rate R (nm/sec) of the silver transparent conductor thin films (3A-3C) is set to be $R = (1/40) \times (T-300) \pm 0.5$, whereby the transparent having a standard deviation of visible light transmittance which is not larger than 5 % in a wave range of from 450 to 650 nm can be produced.

[Selected Drawing] Fig. 1